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SIMPLE METHOD FOR THE PREPARATION OF STANDARD DILUTED GAS MIXTURES IN THE MICROGRAM/cu m TO MILLIGRAM/m RANGE

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SIMPLE METHOD FOR THE PREPARATION OF STANDARD DILUTED GAS MIXTURES IN THE $\mu g \cdot m^{-3}$ TO $mg \cdot m^{-3}$ RANGE

[Méthode simple pour la préparation de dilutions de gas étalon dans le domaine du $\mu g\ m^{-3}$ au $mg\ m^{-3}$]

by

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A device for producing standard diluted gas mixtures in which the constant flow rate is maintained by gaseous viscosity is described. The driving pressure difference is derived from a frictionless mercury ring piston.

The device represents a volumetric primary standard. At the same time, it is also a secondary standard, as the flow rate is known by reference to well-known constants: gas viscosity, cubic dilation constant of mercury, and mass and length measurements.

The apparatus is distinguished by its very simple design and relative insensitivity to temperature variations.

1. Introduction

Gas phase chromatography and various spectrographic techniques, especially the measurement of atmospheric pollutants, make use of the dilution of a chemical species in a carrier gas. Frequently the concentration obtained is assumed to comprise a standard, that is, a value directly based on measurements of weight, volume or flow rate. In this sense, pressurized "standard gases" in steel cylinders are only secondary standards if their composition has been

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determined only by control analyses and not by direct weighing of the components.

In 1959, Saltzman and Gilbert described a device which today is considered classical, in which a viscous flow is maintained through a porous asbestos stopper. Although this method is simple and easy to use, it has the disadvantage of not being "absolute," since preliminary volumetric or analytic calibration is necessary.

In 1962, Goetz and Kallai used a capillary to produce resistance to fluid flow. The pressure differential required for effusion of the gas was provided by a piston whose friction was decreased by the rapid rotary movement of an air turbine, a concept apparently dating back to research performed by Brubach in 1947. The disadvantages of this system are its relative complexity and the fact that the piston is still not completely gas-tight and there may be variations in force parallel to the axis of the piston. (See Rossano and Cooper, 1963.)

The method described below is based on these same principles: viscous flow under the influence of a slight pressure differential provided by a completely impervious frictionless piston. Thus it is valuable to have two simultaneous absolute standards, one for direct volumetry and the other with reference to the viscosity of the gas.

In our opinion, the injection of pollutants regulated by gas viscosity offers yet another decided advantage over methods using evaporation or permeation; while the latter methods require strict maintenance of a constant temperature to ensure constant concentration, there is so little variation in gas viscosity with temperature that the former device can be used without any temperature regulation in the laboratory and with makeshift constant temperature maintenance in the field.

2. Design

The proposed device consists of :

-- a volume of gas in which a frictionless piston ensures a constant pressure differential.

-- a calibrated thermometric capillary tube.

-- a mixing system (see Fig. 1).

The frictionless piston is the "mercury ring" device widely described in physics courses. It is also the basic component in several commerical flowmeters which need not be described in detail here (Nelson, 1973, p. 43).

Plastic (teflon) pistons with a weight per cm^2 of between 1 and 2 g are manufactured by a simple process. The slight pressure differential on the order of $2 \cdot 10^3$ $dyme/cm^{-2}$ generated by the piston is essential for the use of this method, since with a pressure level on this order it is possible to use capillary tubes with diameters of between 0.02 and 0.05 mm. With higher pressure it would be necessary to use smaller diameters, which would be difficult to obtain.

The mercury ring piston is located inside a glass tube corrected to $\pm$ 0.1 mm. $\pm$ 0.1 mm of play is provided so that the piston will float on the mercury ring without touching the wall, even if the axis of the tube deviates from a vertical position by 5°.

The vertical displacement of the piston may be measured down to a few tenths of a millimeter by millimeter graduations etched in the outside of the tube. In our version, we used a graduated tube salvaged from an old, no longer usable cathetometer. With the use of this graduated tube and a small microscope tube with a total magnification of 30 it was possible to estimate the piston displacement down to about 0.05 mm, the respective positions of the cathetometer and the glass tube being fixed. Thus, given the temperature and

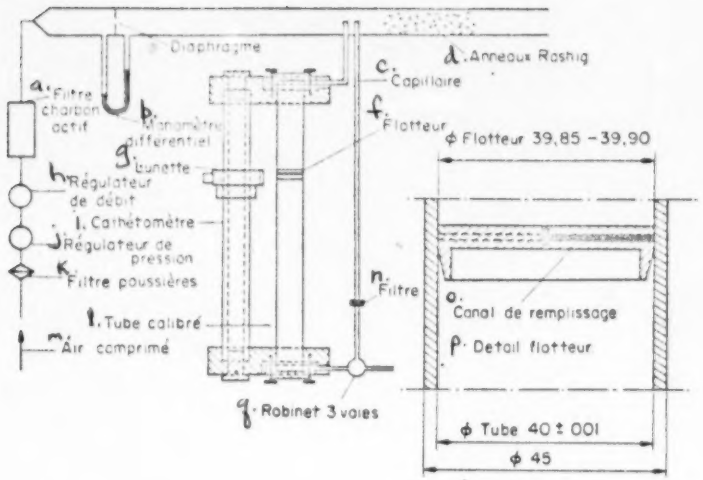

Fig. 1. Structural diagram of device for preparation of standard diluted gas mixtures. At right is a magnified view of the frictionless mercury ring piston.

Key: a. Activated charcoal filter.
b. Differential manometer.
c. Capillary tube.
d. Raschig ring.
f. Float.
g. Ring gauge.
h. Flow regulator.
i. Cathetometer.
j. Pressure regulator.
k. Dust filter.
l. Calibrated tube.
m. Compressed air.
n. Filter.
o. Filling conduit.
p. Detail of float.
q. Three-way valve.

pressure it was possible to determine the flow volume with better than $\pm 1\%$ accuracy, assuming the piston to move 5 cm·24 h^{-1}.

The thermometric capillary tube regulated the gaseous effusion. This could easily be computed by Poiseuille's law, which states that, for air, example, a tube $5 \cdot 10^{-3}$ cm in diameter and 10 cm long will allow the escape of 1.47 $cm^3 \cdot 24\ h^{-1}$ of gas in response to a pressure differential of 2000 dyne/cm^{-2}.

Since the viscosity of air (as well as that of most gases) at a known temperature is a constant defined down to $\pm 0.1\%$, by measuring the flow time of a volume of air under the influence of a known pressure differential it was possible to compute the diameter of the tube with extreme accuracy.

This diameter can also be found by the weight of the quantity of mercury required to fill the tube. This again is a classical physical procedure which need not be described here. However, given the fact that the quantity of mercury required to fill the tube would weigh only about 2.6 mg, the accuracy of the diameter obtained in this way, even with the use of a microbalance, would be much lower than that which could be obtained by the less direct method based on the known viscosity of air.

We recommend a method of calibration which, although less direct, may be more accurate. The capillary tube may be taken from an ordinary medical thermometer. If necessary, after the value of the Centigrade degree has been recalibrated, the length of a degree may easily be measured down to 1%. The container is broken and the mercury it contains is weighed. Since the expansion coefficient of mercury is known to 10^{-5} ($1.8186 \cdot 10^{-4}$ at 20°C), the diameter of the capillary tube may be computed to the desired accuracy. The diameter of the capillary tube of most medical thermometers is around $5 \cdot 10^{-3}$ cm.

It is recommended that capillary tubes much finer than $5 \cdot 10^{-3}$ cm in diameter not be used, for two reasons.

As the diameter approaches the length of the mean free path, the flow would become temporary between the Poiseuille range and the molecular range. Determination of the correction factor to be applied would hinder the accuracy of the absolute calibration.

No disturbances due to the inevitable impurities were noted in capillary tubes $5 \cdot 10^{-3}$ cm or more in diameter. Smaller-diameter tubes frequently become clogged.

In any case, protection of the entrance of the capillary tube with a

membrane filter is recommended. A disk 6 mm in diameter secured between two suitable plastic rings clamped into a cylindrical glass tube is ideal for this purpose. In view of the rate of filtration through the membrane, imperviousness at the edges is not a critical factor. The loss of head caused by the filtration remains negligible for the same reason.

The two independent methods of calibration, by direct volumetry and by reference to the physical dimensions of the tube through Poiseuille's law, naturally furnished results which were in agreement to better than $\pm 0.5\%$. This agreement could be expected in the elementary procedure of determining the viscosity constant of a gas.

The mixing system ensured that the pressure would be the same at the outlet of the capillary tube and above the piston, that is, that the current of pure air for dilution did not exert static pressure (positive or negative) at the outlet of the capillary tube.

We found that the desired effect could be obtained by having the capillary tube (outside diameter approximately 5 mm), whose end was cut at right angles, empty from a radial position into the center of a tube with an inside diameter of at least 35 mm.

The device described may be used directly with some pollutants which do not attack mercury. When several aggressive gases are involved, the method using several intermediate containers, described by Setterlind (1953), may be used to advantage. The area beneath the mercury ring piston and the first containers will be filled with air, the latter to serve as a surge tank. Four to five containers hold the pollutant in its pure state or at the desired dilution, depending on the case. When the containers are connected in series, assuming perfect and instantaneous mixing, the residual concentration of the last container may be computed by means of the equation

given by Setterlind:

$$c_n = c_0\left[1 + \frac{1}{1!}\left(\frac{v_w}{V}\right) + \frac{1}{2!}\left(\frac{v_w}{V}\right)^2 + \cdots \frac{1}{(n-1)!}\left(\frac{v_w}{V}\right)^{n-1}\right]e^{-\left(\frac{v_w}{V}\right)}$$

where

c_n = concentration of gas upon leaving the n^{th} container after extraction of the volume v_w,

c_o = initial concentration in all containers,

V = volume of containers,

v_w = volume of gas extracted from the device, and

n = number of containers.

This equation, which has been confirmed experimentally by Van Sandt (1963) and Nelson (1973, p. 88), furnishes a table of residual concentrations in the containers connected in series, after the extraction of given volumes.

3. Experimental Check

By connecting the upstream end of the capillary tube to a recording manometer, it was found that the differential pressure displayed was maintained with less than 1% deviation and that this occurred independently of variations in temperature and barometric pressure in the laboratory over several weeks of testing.

Another, volumetric check revealed that the flow rate per 24-hour period remained strictly constant over the same number of weeks.

A number of analytical checks on SO_2 and NO_2, using various automatic devices and manual analytic methods, revealed variations in concentration ranging to a maximum of 1%. It should be noted that chemical analysis of the diluted mixtures only showed that the system was functioning satisfactorily. There was no need to confirm its standard nature by procedures (dilution flow

rate: chemical or physicochemical analysis) whose accuracy is seldom as high as 1%.